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A MODEL OF ION EXCHANGE AND WATER PERCOLATION IN FOREST SOILS UNDER ACID PRECIPITATION

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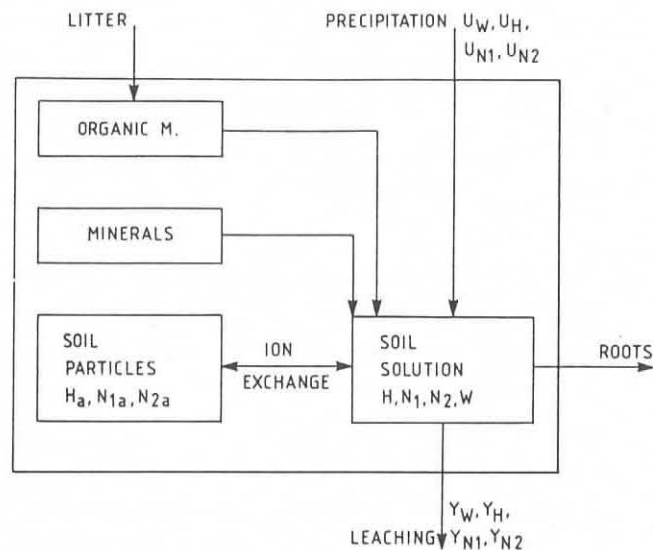
ABSTRACT

The soil profile is divided for the purpose of the study into layers 1 cm thick. The monovalent and divalent cations are treated separately in each layer. The flow of cations between the different layers is controlled by the movement of water and the ions in it. The values of the parameters are estimated using theoretical argumentation. The soil profile is assumed to be in equilibrium before the acid load is applied. The time constants of the cation exchange process are approximated. The equilibrium requirement and the time constants provide the information necessary for the estimation of the values of the parameters. The model is tested using lysimeter experiments with artificial acid rain.

1. INTRODUCTION

The effect of acid rain on soil takes place through weathering of minerals, microbial activity and cation exchange. The possibility of permanent change in the state of forest soils is most apparent in connection with the leaching of nutrients due to acidification of soil, where cation exchange is believed to play a major role. The leaching process can remove nutrients originally available for plants that are not recycled naturally, and another irreversible change can take place by the activation of certain poisonous processes such as release of aluminium compounds under acid conditions.

In boreal coniferous forests the humus is relatively acid and the bulk of the decomposers are fungi that are rather insensitive to acidity (Trudgill 1977). This indicates that the impact of acid rain on micro-organisms is less significant than in more basic soil types. Secondly, the organic layer is thin and the buffer capacity of the soil is poor due to relatively low Ca content in the minerals. These factors indicate that in boreal coniferous forests the leaching of nutrients from the soil can be an important consequence of acid deposition.



STATE $(H, N_1, N_2, N_{1a}, W)^T$
 (WEIGHTS PER UNIT WEIGHT OF SOIL)
 H, H_a HYDROGEN
 N_1, N_{2a} MONOVALENT CATIONS (K^+, Na^+)
 N_2, N_{2a} DIVALENT CATIONS (Ca^{2+}, Mg^{2+})
 W WATER

Figure 1. Restriction of the system.

The present paper introduces a simulation model of the acidification of soil, based on cation exchange and water percolation through the soil. The model produces an estimate of the change of soil acidity in time when the rate and acidity of precipitation are given. The work is part of a project dealing with the effects of air pollutants due to energy production on trees, carried out at Helsinki University.

2. THE MODEL

Fig. 1 illustrates the most important processes associated with soil nutrient status and acidity (cf. Trudgill 1977). Nutrients occur in the soil in four different states: in water as soluble ion (N_i), adsorbed on the surface of

soil particles (N_{ia}), as chemical components of minerals (N_m) and soil organic matter (N_{io}). Hydrogen occurs either in soil water as free soluble ions (H^+) or adsorbed on the surface of soil particles (H_a). The arrows in Fig. 1 describe nutrient and hydrogen flows between these compartments and between the soil system and its environment. These flows only occur in the presence of water (W), which can either stay in the system or percolate through it from the surface to the lower soil layers.

The aim of the study was to produce a model that can be utilized in analysing the effects of acid deposition on this system. The most important dynamic properties of the system are associated with the ion exchange process, provided that this is connected with the flow of water through the system. Therefore, the present preliminary version of the model only incorporates these two processes, ignoring decomposition of soil organic matter, weathering of minerals and nutrient uptake by plants. This simplification corresponds to the assumption that these three material flows approximately cancel each other. The state of the soil, X, is therefore defined as follows:

$$X = (H, N_1, N_2, H_a, N_{1a}, N_{2a}, W)^T$$

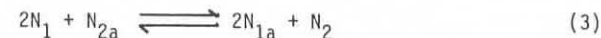
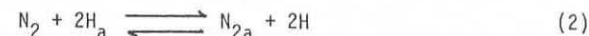
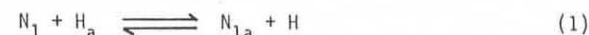
H amount of hydrogen ions in soil solution
 N_1 amount of monovalent cations in soil solution
 N_2 amount of divalent cations in soil solution
 H_a amount of hydrogen ions adsorbed on soil particles
 N_{1a} amount of monovalent cations adsorbed on soil particles
 N_{2a} amount of divalent cations adsorbed on soil particles
 W amount of water

The amounts of ions are expressed in millimoles (mmol) and that of water in liters (l), both per unit volume of soil.

2.1 Ion exchange

Ion exchange is treated analogously to the process occurring in a chemical buffer solution where ions with the same valence behave identically.

Two types of cations are considered: N_1 and N_{1a} represent monovalent cations such as K^+ and Na^+ , while N_2 and N_{2a} represent divalent ones such as Ca^{2+} and Mg^{2+} . The following reaction equations are obtained: (cf. Brustad et. al. 1979).



The error due to combining cations with the same valence is minor provided either that they behave similarly in the exchange process or that one of the ions clearly dominates the others. In leaching experiments by the Norwegian

SNSF project, the concentrations of Ca^{2+} and Mg^{2+} changed similarly when water was percolating through a soil profile. The changes of K^+ and N_1 concentrations have usually been similar to each other (Brustad et. al. 1979). The experiments carried out in our project support these results. The positions of the ions with respect to nutrient uptake is different however, and if more detailed results are aimed at, different cations will have to be considered separately.

The dynamic equations of the model are formed on the basis of Eqs. (1)-(3). We assume that the reaction rate is proportional to the amounts of the reacting ions. The differential equations formed on the basis of Eq. (1) for H and N_1 are hence:

$$\frac{dH}{dt} = \alpha_1 H N_{1a} + \alpha_2 H_a N_1 \quad (4)$$

$$\frac{dN_1}{dt} = \alpha_1 H N_{1a} - \alpha_2 H_a N_1 \quad (5)$$

where α_1 and α_2 are constant parameters.

Eqs. (2) and (3) are treated in a similar way, and the resulting derivatives are summed up to give a model for the complete system. The equations for H_a , N_{1a} and N_{2a} are obtained by changing the sign of the respective soluble ion derivatives.

The following set of equations is obtained:

$$\frac{dH}{dt} = -(\alpha_1 N_{1a} + \alpha_3 H N_{2a})H + (\alpha_2 N_1 + \alpha_4 N_2 H_a)H_a$$

$$\frac{dN_1}{dt} = -(\alpha_2 H_a + \alpha_5 N_1 N_{2a})H_1 + (\alpha_1 H + \alpha_6 N_2 N_{1a})N_{1a}$$

$$\frac{dN_2}{dt} = -(\alpha_4 H_a^2 + \alpha_6 N_{1a}^2)N_2 + (\alpha_3 H^2 + \alpha_5 N_1^2)N_{2a}$$

$$\frac{dH}{dt} = -\frac{dH}{dt} \quad (6)$$

$$\frac{dN_{1a}}{dt} = -\frac{dN_1}{dt}$$

$$\frac{dN_{2a}}{dt} = -\frac{dN_2}{dt}$$

all state variables and parameters non-negative.

2.2 Transport of ions by water

Consider the flow rate of water per unit surface area. In the top layers of soil horizontal movements of water are negligible, and from the point of view of leaching it is only the vertical dimension that matters.

The model assumes that the water content of the soil never goes below field capacity, which corresponds to the watering experiment in the project and the situation in the field during a rainy period. It is further assumed that the surplus of water is transported down the profile with a specific (constant) flow rate. The profile is divided into n horizontal layers, assuming a complete mixing of water and its solutants within each layer. The ions are hence transported down the soil profile whenever there is a downward flow of water. A summary of the water flow and ion transport model is presented in Fig. 2.

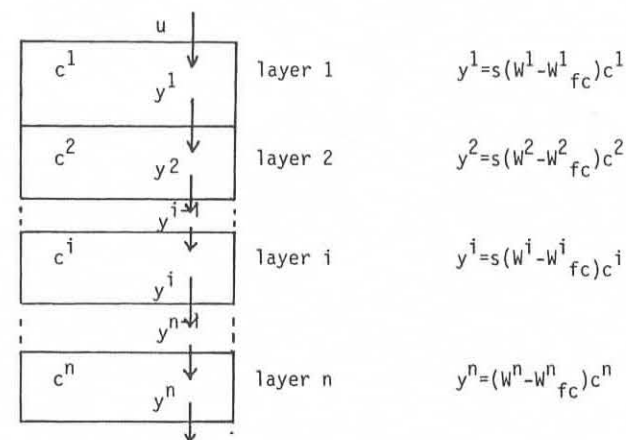


Figure 2. Description of the model of water percolation. Symbols:

- u : input (water and ions)
- c_i : vector of ion concentration in layer i
- y_i : output from layer i (water and ions)
- W_i : amount of water in layer i
- W_{fc}^i : field capacity corresponding to layer i
- s : parameter

2.3. Mathematical summary of the model

Denote the time derivatives of H , N_1 and N_2 in Eq. (6) by DH , DN_1 and DN_2 , respectively. Associate a label k ($1, \dots, n$) to each soil layer, the flow of ions i with water into the layer k by u^k and the outward ion flow from the layer by y^k . Combining the submodels for ion exchange and water

flow gives the following differential equations for hydrogen and exchangeable cations in layer k (the dot refers to time derivatives):

$$\begin{aligned}\dot{H}^k &= DH^k + u_H^k - y_H^k \\ \dot{N}_1^k &= DN_1^k + u_{N1}^k - y_{N1}^k \\ \dot{N}_2^k &= DN_2^k + u_{N2}^k - y_{N2}^k \\ \dot{H}_a^k &= -DH^k \\ \dot{N}_{1a}^k &= -DN_1^k \\ \dot{N}_{2a}^k &= -DN_2^k \\ u_i^k &= y_i^{k-1}, \quad 1 \leq k \leq n\end{aligned}$$

There are seven parameters in the model, which have been determined combining a theoretical equilibrium analysis with some reaction rate estimates found in the literature. The differential equations have been solved numerically using the Runge-Kutta integration method.

3. RESULTS AND DISCUSSION

Simulations of the model have been carried out with initial hydrogen and nutrient ion concentrations corresponding to the values of VT-type pine forests, which is a common poor forest type in Finland (Table 1). The parameter values applied are listed in Table 2.

Table 1. Ion concentrations in initial state in a 1 cm soil layer.

Soil solution		
- amount of hydrogen ions	H	1) 0.47 mmol/m ²
- amount of monovalent cations	N ₁	1.30 "
- amount of divalent cations	N ₂	0.48 "
Adsorbed ions		
- hydrogen	H _a	1200.00 "
- monovalent cations	N _{1a}	50.00 "
- divalent cations	N _{2a}	200.00 "
Amount of water (field capacity)	W _{fc}	7.5 l/m ²

1) Corresponds to pH 4.2

Table 2. Parameter values.

α ₁	0.729 · 10 ⁻⁵
α ₂	0.110 · 10 ⁻⁶
α ₃	0.595 · 10 ⁻⁵
α ₄	0.380 · 10 ⁻⁹
α ₅	0.269 · 10 ⁻⁶
α ₆	0.758 · 10 ⁻⁷
s	4.0

ION CONCENTRATIONS IN LEACHATE

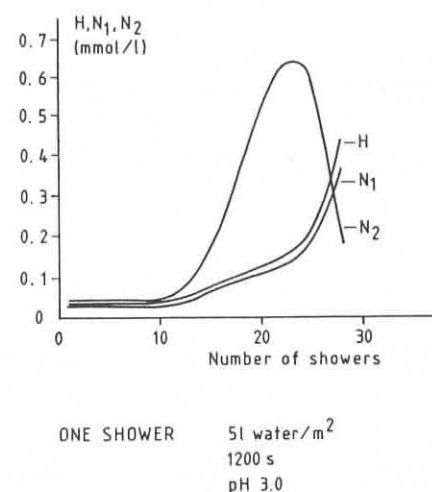


Figure 3. The simulated time course of ion concentrations in water flow through a 25 cm soil profile subject to 30 successive acid showers. The amount of water per shower is 5 l/m² over a 1200 s period and the pH value is 3.0.

Fig. 3 shows the simulated time course of ion concentrations in water flow through a 25 cm soil profile subject to 30 successive acid showers. The amount of water (pH 3) per shower is 5 l/m² over a 1200 s period. In 20 showers the concentration of divalent cations reaches a maximum and starts to decline, while the concentrations of hydrogen and monovalent cations keep increasing till the end of the simulation. However, N₁ will achieve a similar peak if the simulation time is extended. This reflects the replacement of nutrient cations by hydrogen ions on the surface of soil particles in cation exchange, which takes place until all the exchangeable nutrients have leached out.

ION CONCENTRATIONS IN SOIL SOLUTION

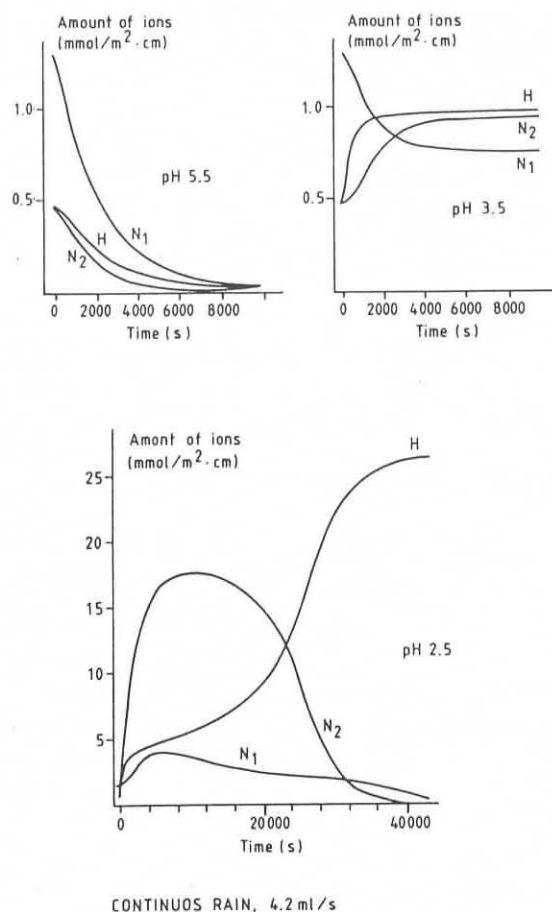


Figure 4. The simulated time course of ion concentrations in the soil solution when the soil is exposed to continuous acid precipitation. The input rate of water is 4.17 ml/s, applied over a period of 8000 s. The acidity of the precipitation is shown in the figure.

Whether or not it is the divalent cations that get exhausted first depends upon the subject soil, represented in the model by parameter values.

Fig. 4 compares the development of ion concentrations in soils exposed to different degrees of continuous acid precipitation. The input rate of water is 4.17 ml/s, applied over a period of 8000 s.

There is rather a distinct limiting acidity (pH 2.5 - 3.0) at which the buffer capacity of the system seems to collapse, resulting in a rapid increase in the amount of H^+ ions in the solution and a nearly complete vanishing of nutrient cations. This is consistent with the experiments carried out in our project (Katainen and Heikkilä 1984).

The relationship between the total amount of input hydrogen ions and the rate of input was analysed by comparing two simulations where identical amounts of hydrogen ions were applied at different rates. The result was that leaching was more efficient in the high rate simulation, indicating that the cation exchange process behaves exponentially with respect to H^+ concentration. In summary, the model seems to function satisfactorily and hence to provide an applicable tool for further analyses. The most significant simplification was to ignore nutrient uptake by plants, and the results should be analysed bearing this in mind. The model apparently overestimates cation leaching during periods of high root activity, when the surplus of nutrients released by acidification is taken up by the roots. Considering the soil to be in field capacity has a similar effect - during dryer periods there is little throughflow of water and hence little output of cations. On the other hand, when the soil is dry the concentrations of elements are higher and the exchange process is more intensive, increasing the rate of change due to acidification. If there is a potential for the weathering of aluminium compounds, for instance, the model predicts it will be higher during dry periods.

It is fairly easy to include a simple treatment of nutrient uptake and changing soil water content in the model, which will give more information of the significance of acid precipitation for forest soils. In order to incorporate tree growth, however, one needs a far more complicated approach. The point where the lack of knowledge seems to condense is the dynamics of root functioning in relation to soil characteristics. However, since this approach is restricted to mineral nutrients only, it is best utilizable trying to predict the rate of soil acidification as such. This is interesting for instance from the point of view of the poisonous reactions caused by the release of aluminium which only occurs under highly acid conditions. If the effects on forest flora are to be thoroughly examined, nitrogen and hence soil organic processes should be incorporated.

REFERENCES

- Brustad, K., Christopherson, N., Njos, A. and Seip, H. M. 1979. Simulation of flow patterns and ion-exchange processes in a series of soil percolation experiments. - Oslo-As, SNSF-project, IR 41/79.

Katainen, H-S. and Heikkilä, E. 1984. On the effect of acid deposition on the nutrient economy of Scots pine. This volume.

Trudgill, S. T. 1977. Soil and vegetation systems. - Oxford, Oxford University Press.

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